CATHODO-LUMINESCENCE SPECTRA OF INDIAN CALCITES, LIMESTONES, DOLOMITES AND ARAGONITES

By BIBHUTI MUKHERJEE

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Plates X-A and X-B

ABSTRACT. The cathodo-luminescence spectra of Indian calcites, limestones, dolomites and aragonites in the visible and the ultraviolet regions were studied using a direct vision spectrograph and a Fuess quartz spectrograph. On inspection of the line-like bands, it was ascertained that the rare-earth activators for luminescence were in calcites Sm, Dy, Eu, and Er, in dolomites Dy and probably Sm, Eu, and in aragonites only Dy. The rare-earths with even atomic number were the chief activators for luminescence with the exception of Eu of odd atomic number. It was definitely ascertained that when rare-earths were present in calcite in optimum quantity for strong activating ability, the luminescence spectrum of Mn in the visible region was totally suppressed by the activating action of rare earths. Below this optimum quantity both rare-earths and manganese acted as activators for luminescence. The position of the line-like band of rare-earth in the luminescence spectrum of calcite, dolomite and aragonite was the same as that in fluorite, which indicated that the limitations placed upon the activating rare-earth atoms by the neighbouring atoms were the same in all these minerals It was found that strontium and thallium showed no characteristic luminescence because of the strong activating ability of manganese when present in traces in CaO as diluent.

INTRODUCTION

The luminescence of calcites was known for many years (Gmelins, 1938). Becquerel (1889) at first found that the luminescence of calcites was due to manganese contained in them. Nichols, Howes and Wilber (1918) attributed the cathodo-luminescence of calcites to manganese present in traces. Tanaka (1924) studied the cathodo-luminescence of calcites and proved that the chief active agent for luminescence was manganese and the other active agents were thallium, dysprosium, samarium, yttrium. Yoshimura (1934) observed that the cathodo-luminescence spectra given by various calcites consisted of a broad band in the red to yellowish green region having two intensity maxima at 6050Å-5950Å and near 6310Å which is due to the presence of manganese, but no line-like bands due to rare-earths. Since the emissions due to rare-earths could not, however, be observed in the luminescence spectra the specimens were sufficiently ignited for several hours to convert them into oxides, and then the luminescence spectra of only two ignited specimens (out of five) showed the additional line-like bands due to rare-earths appearing overlapped on the broad band due

to Mn. The rare-earth activators for luminescence of these two ignited specimens were Pr, Eu, Dy and Tb.

Tanaka (*loc. cit.*) studied the cathodo-luminescence of limestones, dolomites, aragonites and found that the active agents for luminescence were Mn, Tl, Dy in limestones, Sr, Mn, Cu in aragonites and Mn, Dy, Y in dolomites. In the previous investigation on the cathodo-luminescence spectra of Indian flourites, the author (Mukherjee, 1948) pointed out that according to Urbain (1909) La, Ce, Y and Yb whose salts are colourless and devoid of absorpation spectra were found not to exhibit any such luminescence. The author (1948) concluded that though Mn was present in all the chemically decomposed specimens of fluorite the characteristic Mn-band in the visible region was suppressed in the luminescence spectra by the strong activating ability of rare earths.

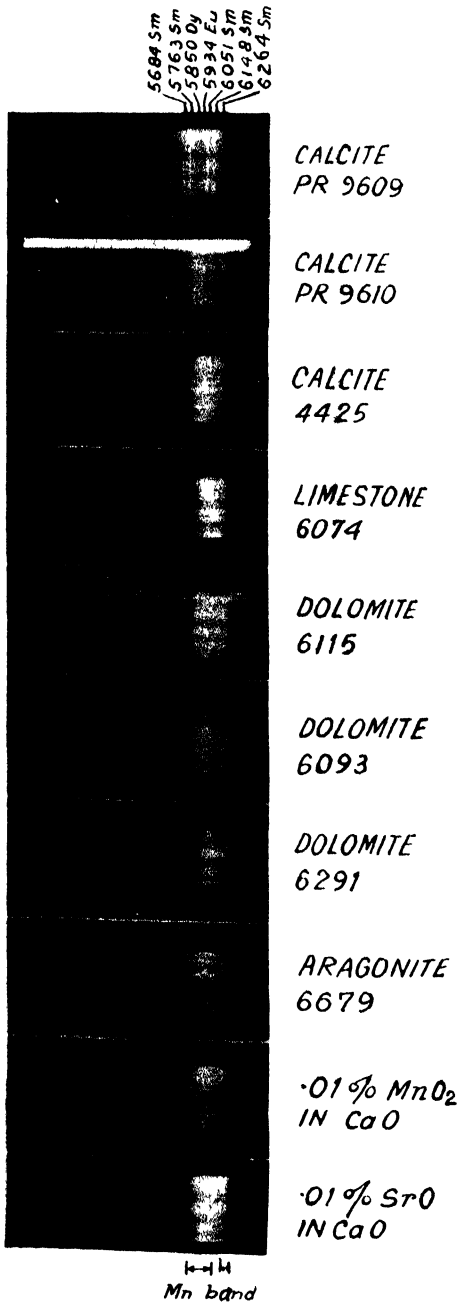
The object of the present investigation was to determine the activators for luminescence in calcites, limestones, dolomites, aragonites and to trace the influence of other impurities on the activating ability of rare-earths present in the specimens.

EXPERIMENTAL

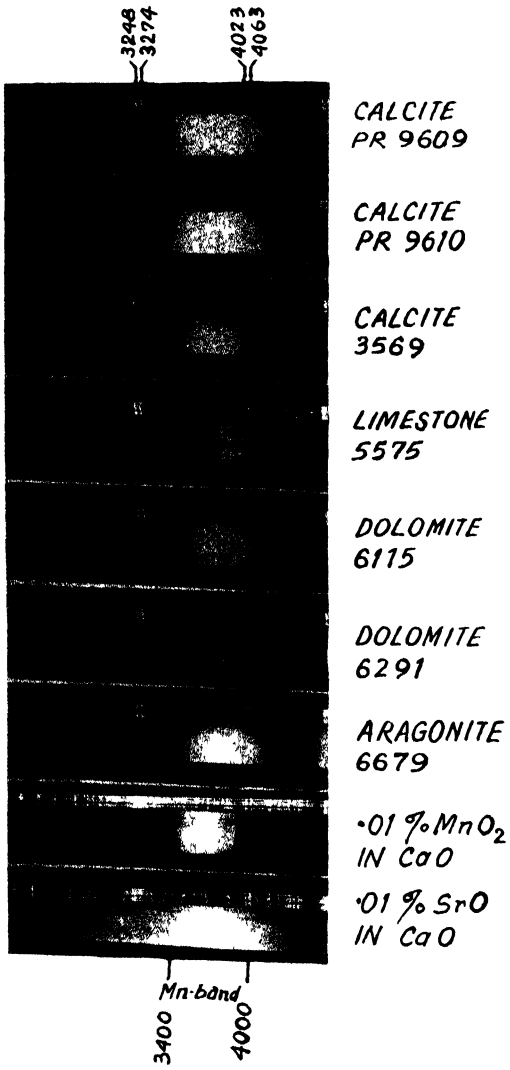
The qualitative arc spectrographic analysis of calcites, limestones, dolomites and aragonites was carried out at 9 amps. 220 volts with a E_1 quartz spectrograph. The presence of rare-earths could not, however, be detected in any of the specimens. All the specimens contained traces of manganese. Traces of strontium was present in aragonite No. 6679. The method of cathodo-luminescence was applied for the study of rare-earths in these specimens.

In the experiment, the arrangement for generating the cathode rays and the method adopted for exciting the specimens in the tube was the same as that used in the previous investigation on Indian fluorites (Mukherjee, *loc. cit.*). Each of the specimens of calcite, limestone, dolomite and aragonite was powdered and heated for 5 minutes in a muffle furnace at nearly 800°C—1000°C. This ignited specimen was exposed to cathode rays in the tube just after the heat treatment. The best condition for excitation of the specimen was at 4000V, the current in the tube being kept at 4-5 mA. Direct vision spectrograph and Fuess quartz spectrograph were used for taking spectrograms both in the visible and the ultraviolet regions. The time of exposure in the direct vision spectrograph was 2-10 minutes, ultra-sensitive panchromatic plates being used. In the quartz spectrograph the time of exposure was 5-12 minutes.

The identification of the line-like bands in the luminescence spectra of the specimens, observed under a 'comparator' of nearly 10 times magnification, was carried out referring to Urbain's data for the different system of rare-earth oxide in calcium oxide (R_2O_3-CaO). Standard mixtures of



Cathodo - Luminescence Spectra.



Cathodo - Luminescence Spectra.

nearly 0.01% manganese oxide in CaO, 0.01% strontium oxide in CaO and 0.01% thallium oxide in CaO were prepared and their cathodo-luminescence spectra were photographed using both the spectrographs.

TABLE I

Colour of luminescence of calcite, limestone, dolomite, aragonite and activators for luminescence.

No. of specimen	Locality	Colour of luminescence	Activators of luminescence
Calcite			
PR 9609	Giridih	Yellowish white	Sm*, Dy, (Eu), Mn
PR 9610	Udaipur	Greenish white	Sm, Dy, Eu, (Er)
PR 9602 (2)	Sinolu State	Orange yellow	No rare earths, only Mn
PR 9602 (4)	,,	,,	,,
3569	Beawar & Sendu Rly. Stn. B.B. & C.I. Rly.	,,	,,
11	Nr. Gadhagra	,,	,,
5530	Poonera, Ajmer Dt	,,	,,
4125	2 miles W. of Barna, Kishengarh State, Rajputana,	,,	,,
4377	Mogok Sub. Div Upper Burma	,,	,,
Limestone			
5387	Pentalgudi, Ramnad, Madura.	Deep orange	No rare-earths, only Mn
5413	Mankaria Village, Kekri Dt., Ajmer.	Yellow	,,
5575	Raipur, Gangpur State, Orissa.	Pale red, yellow tinge	,,
6074	Myli River, Palamaw, Lohardaga Dt, Bihar	Pale red, orange tinge	,,
6296	Salt Range, Punjab	,,	,,
7126	Someswar Range, Bihar.	Organge-yellow	,,
Dolomite			
6115	Marble Rocks, Jubbulpore, C.P.	Yellowish white, Violet tinge	Dy*, (Sm), (Eu), Mn
6093	Nr. Saiduwali, Salt Range, W. Punjab.	Yellow	Dy, Mn*.
6291	From saline series, Salt Range, W. Punjab.	Orange-yellow	No rare-earths, only Mn ,,
4727	Raipur, Gangpur State	Pale red	
1200	Jhanbeda hill deposits, Gangpur State	Orange-yellow	,,
Aragonite. 6679	24 miles N.W. of Nokhundi, Baluchistan.	Yellowish-white	Dy, Mn

The * mark indicates the chief activator of luminescence.

TABLE II

Wavelengths of the line-like bands in the visible region observed in the luminescence spectra of calcite, dolomite and aragonite. λ in 1 Å.

Calcite		Dolomite		Aragonite	Rare-earth-in CaO Urbain's data
PR 9609	PR 9610	6115	6093	6079	
6336 m	6336 s	6330 } s, b	5956 } s, b	5956 } ss, b	6340 Eu
6264 s	6264 s	6240 }	5875 }	5875 }	6265 Sm
6148 ss	6148 s	6148 m	5850 }	5850 }	6245 Eu
6051 ss	6051 s	6051 s			6155 Eu
5934 s	5934 s	5956 } c, b			6150 Sm
5850 s	5850 s	5934 }			6052 Sm
5763 ss	5763 s	5875 } s, b			5958 Dy
5684 ss	5684 s	5850 }			5930 Eu
5550 f	5598 m	5826 s			5877 Dy
*5182 f	5556 m	5763 s			5848 Dy
	5492 ss	5681 m			5830 Dy
	*5482 f				5762 Sm
	5403 f				5683 Sm
	5358 f				5603 Er
	5178 f, b				5561 Sm
	4896 f				5550 } Eu
	4850 m				5195 }
	4718 f				5486 Sm
					5405 Eu
					5365 Eu
					5355 Er
					5180 Eu
					4900 – 4882 Dy
					4845 Dy
					4728 Dy
					4720 Eu

The intensities of the line-like bands are expressed by the symbols, ss = very strong ; s = strong , m = medium ; f = faint , b = broad *Strong line of discharge.

The calibration of the scale in the direct-vision spectrograph due to small dispersion and broad width of the slit was subject to an error of 6Å. Some of these lines were also coincident with faint lines of discharge.

INTERPRETATION OF RESULTS

Calcite.—The luminescence spectra of almost all calcites were found to be broad banded (from 6330 Å to 6150 Å and 6050 Å to 5560 Å). Such a broad band was observed in the luminescence spectrum of 0.01% manganese oxide in CaO (Mukherjee, 1948). The luminescence spectra of all calcites (PR 9609, PR 9610, 3569, etc.) also showed a broad band in the ultraviolet region (from 4000 Å to 3400 Å). This broad band was proved to be due to manganese acting as an activator in CaO as diluent (Mukherjee, 1948). It can, thus, be ascertained that Mn acted as strong activator for luminescence in calcites.

In the luminescence spectrum (visible region) of calcite No. PR 9609, it was observed that line-like bands of rare-earths were superimposed on the

broad band of manganese. In this calcite, rare-earths acted as activator for luminescence along with manganese. In the luminescence spectrum (visible region) of calcite No. PR 9610, only the line-like bands of rare-earths appeared, there being practically no broad band due to Mn. But the luminescence spectrum of this calcite in the ultra-violet region showed the characteristic broad band due to Mn, which proved that the Mn-band was suppressed only in the visible region by the activating action of rare-earths. From all these considerations, it is definitely ascertained that when rare-earths are present in calcites in optimum quantity for strong activating ability, the luminescence spectrum of Mn in the visible region is totally suppressed by the activating action of rare-earths. But below this optimum quantity (as in calcite No. PR 9609) both rare-earths and manganese act as activators for luminescence.

The rare-earth activators for luminescence in calcites were Sm (specially in specimen No. PR 9609), Dy, Eu; and probably Er also acted as activator.

Limestone.—The luminescence spectra of all limestones consisted of characteristic broad bands of Mn both in the visible and the ultra-violet regions. The Mn-band in the visible region was much stronger than that in the ultra-violet region. The line-like bands of rare-earths were not observed in the luminescence spectra of these specimens. Manganese alone acted as activator for luminescence in limestones.

Dolomite.—In the luminescence spectra of dolomites Nos. 6115 and 6093, Dy acted as the chief activator for luminescence along with Mn. In specimen No. 6115, Sm and Eu also appeared to act as activators. In the luminescence spectra of all specimens of dolomite (6115, 6093, 6291, etc.), the characteristic Mn-band in the ultra-violet region appeared strongly as was found in calcites.

Aragonite.—The luminescence spectrum of aragonite No. 6679, consisted of strong broad band of Mn in the visible region upon which was superimposed the characteristic line-like bands of Dy. The characteristic Mn-band in the ultra-violet region was also present. Thus it is ascertained that Dy acted as activator for luminescence in aragonite along with Mn.

It is interesting to note that rare-earths with even atomic number (Sm 62, Dy 66, Er 68) were the chief activators for luminescence of these minerals with the exception of europium (Eu 63) of odd atomic number. The presence of Gd could not, however, be ascertained in any of these minerals. The position of the line-like band of rare-earth in the luminescence spectrum of calcite, dolomite and aragonite was the same as it was found in fluorite (Mukherjee, 1948) which indicated that the limitations placed upon the activating rare-earth atoms by the neighbouring atoms were the same in all these minerals.

DISCUSSION

Tanaka (*loc. cit.*) ascertained that thallium also acted as activator for luminescence in calcite along with manganese and rare-earths. In the present investigation the luminescence spectrum of 0.01% thallium oxide in CaO was studied and it was found that only the characteristic Mn-bands appeared both in the visible and the ultra-violet regions. According to Urbain (1911) there was no chemically pure calcium salt free from manganese. Thus it can be ascertained definitely that in presence of even minute traces of Mn, thallium does not show any characteristic luminescence because of the strong activating ability of manganese in CaO as diluent.

Tanaka (1924) also ascertained that strontium and probably copper acted as activator for luminescence along with manganese in aragonites. In the present investigation the luminescence spectra of 0.01% and 0.1% strontium oxide in CaO were studied and it was found that only the characteristic Mn-band appeared both in the visible and the ultraviolet regions. Thus it is ascertained that strontium (though present in aragonite No. 6679) does not show any characteristic luminescence because of the strong activating ability of manganese (present always in traces) in CaO as diluent.

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UNIVERSITY COLLEGE OF SCIENCE AND TECHNOLOGY,
92, UPPER CIRCULAR ROAD, CALCUTTA.

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